COMBUSTION ANALYSIS
COMPLEX PROBLEMS
(Empirical Formula/ Molecular Formula)

* This particular type of calculation has a number of standard steps that are the same on every occasion, these being the steps that isolate the carbon and hydrogen content of an unknown compound. Oxygen can never be calculated directly as, in combustion, there is an external source of oxygen apart from that in the compound. Oxygen must be determined by calculating the ***total mass of all component parts*** of the compound and then ***subtracting*** this from the ***mass of the compound that was burnt***, this will leave you with the mass of oxygen that was actually in the compound and not simply present in the air in which the combustion took place.

In the T.E.E. there is often an ***extra element*** that is included in the unknown compound to be combusted so that some non-standard steps are required.

***** You should always bear in mind that whatever elements are in the compound, they are being oxidised or burnt in oxygen- these mean the same thing! The products will be the oxide of carbon (CO_2), the oxide of hydrogen (H_2O) and the oxide of whatever other element is present. For example- if sulfur had been in the compound then SO_2 would be the oxide; nitrogen may produce NO or NO_2; silicon may produce SiO_2 etc.***

The first part of these questions will commonly ask you to calculate the ***Empirical Formula*** (lowest whole number ratio) but a second element is usually included that involves calculation of the ***Molecular Formula***. The molecular formula (M.F.) is always a whole number multiple of the empirical formula (E.F.) or may even be the same as the empirical formula. To decide what factor relates the two, you will have to calculate the Molar Mass (Molecular Mass) of the ***true*** molecule and compare this to the mass of the empirical formula (E.F.W.). To do this you will frequently have to incorporate your knowledge of the gas equation : PV = nRT as a means to calculating the moles of a vaporised sample of the unknown compound.

<u>TYPE EXAMPLE:</u>

A pure substance 'A' is a colourless liquid boiling at 229 ^{0}C and contains carbon, hydrogen, silicon and oxygen.
When 1.0640 g of 'A' was burnt in current of dry oxygen, 1.462g of carbon dioxide and 0.894 g of water were produced. The solid which remained consisted of 0.832g of silicon dioxide.

(a) Calculate the EMPIRICAL FORMULA of 'A'.

(b) At 150 ^{0}C and 2.0 kPa pressure, 0.0138g of 'A' evaporated (vaporised) to occupy a volume of 67 mL. Calculate the molecular weight (Molar Mass) of 'A'. Use this value to determine the MOLECULAR FORMULA of the compound.

(c) A nuclear magnetic resonance spectrum for 'A' showed all the hydrogen atoms to be in methyl groups. Suggest a STRUCTURAL FORMULA for 'A'.

** Adapted from T.E.E. 2000, Qu 2 Calculation.*

SOLUTION

(a) EMPIRICAL FORMULA DETERMINATION:

$$\underset{1.0640g}{C_xH_yO_zSi_p} + O_2 \rightarrow \underset{1.462g}{CO_2} + \underset{0.894g}{H_2O} + \underset{0.832g}{SiO_2}$$

Step 1: Carbon Determination (Standard)

* CO_2
12.01
16.00 x 2
44.01 $gmol^{-1}$

$n(CO_2) = \frac{m}{M}$
$= \frac{1.462}{44.01}$
$\therefore n(CO_2) = 0.03322 mol$

$n(C) = n(CO_2)$
$\therefore n(C) = 0.03322 mol$

Step 2: Hydrogen Determination (Standard)

* H_2O
1.008 x 2
16.00
18.016 $gmol^{-1}$

$n(H_2O) = \frac{m}{M}$
$= \frac{0.894}{18.016}$
$\therefore n(H_2O) = 0.04962 mol$

$n(H) = 2 \times n(H_2O)$
$n(H) = 2 \times 0.04962$
$\therefore n(H) = 0.09925 mol$

Step 3: Extra Element (non- standard)

* SiO_2
28.09
16.00 x 2
60.09 $gmol^{-1}$

$n(SiO_2) = \frac{m}{M}$
$= \frac{0.832}{60.09}$
$\therefore n(SiO_2) = 0.01385 mol$

$n(Si) = n(SiO_2)$
$\therefore n(Si) = 0.01385 mol$

Step 4: Mass Determinationof all Components (Standard)

$m(C) = n(C) \times M$
$= 0.03322 \times 12.01$
$\therefore m(C) = 0.3989g$

$m(H) = n(H) \times M$
$= 0.09925 \times 1.008$
$\therefore m(H) = 0.1000g$

* *Determination of extra element is no*

$m(Si) = n(Si) \times M$
$= 0.01385 \times 28.09$
$\therefore m(Si) = 0.3890g$

Step 5: Determination of Oxygen (Standard)

m(O) = Total Mass of Compound Burnt - m[C + H + *Si]
= 1.0640 - [0.3989 + 0.1000 + 0.3890]
= 1.0640 - [0.8879]

∴ m(O) = 0.1761g ***Extra Element varies if indeed there is one!**

$$n(O) = \frac{m}{M} = \frac{0.1761}{16.00}$$

∴ n(O) = 0.01101 mol

Step 6: Mole Ratio (Standard)

MOLE RATIO	C	:	H	:	O	:	Si	* (Extra element varies!)
	0.03322	:	0.09925	:	0.01101	:	0.01385	
**Division by smallest amount to simplify*	$\frac{0.03322}{0.01101}$	:	$\frac{0.09925}{0.01101}$	:	$\frac{0.01101}{0.01101}$	:	$\frac{0.01385}{0.01101}$	
**Multiplication by a factor to bring any number with a fraction to the nearest WHOLE NUMBER!*	3.02	:	9.01	:	1.00	:	1.26	
	(3.02	:	9.01	:	1.00	:	1.26*) x 4	
	12	**:**	**36**	**:**	**4**	**:**	**5**	

∴ Empirical Formula = $C_{12}H_{36}O_4Si_5$

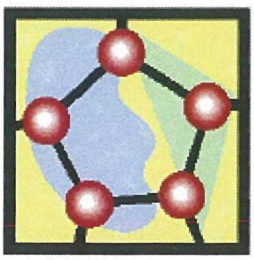
(b) MOLECULAR FORMULA DETERMINATION:

0.0138g Evaporated ⇨

Molecular Weight (Molar Mass)/ Molecular Formula Determination (Standard)

P = 2.0 kPa
V = 67 mL = 0.067 L
n = ?
R= 8.315 $JK^{-1}mol^{-1}$
T= 150 ^{0}C = 150 + 273 = 423K

** Always use "P" in kPa; "V" in Litres and "T" in Kelvin which allows you to use the same value for "R"!*



PV = n RT

$$\therefore n = \frac{PV}{RT} = \frac{2 \times 0.067}{8.315 \times 423}$$

∴ n(Compound) = 0.00003809 mol

If these are in diferent units then convert first:
1 atm = 760 mm of Hg = 101.3 kPa
Kelvin = Celcius + 273

$$n(\text{Compound}) = \frac{m}{M}$$

$$\therefore M(\text{Compound}) = \frac{m}{n} = \frac{0.0138}{0.00003809}$$

∴ M (Compound) = 363.16 $gmol^{-1}$

Empirical Formula Weight Calculation/ Comparison with Molecular Weight(Standard)

E.F.W. = $C_{12}H_{36}O_4Si_5$

= (12 x 12.01) +

(36 x 1,008) +

(4 x 16) +

(5 x 28.09)

= 384.9 g ⟺ ** *M.F.W. (Molar Mass Compound) = 363.16 g

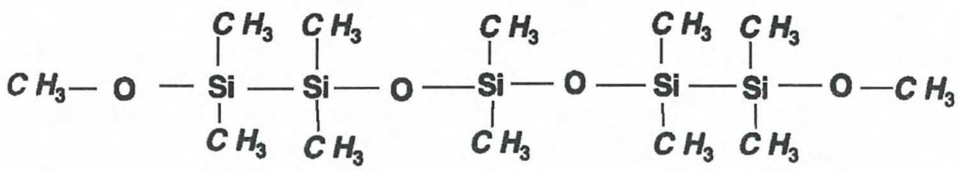
** *These two values are not identical but are close to equivalent, given the inevitable experimental errors associated with this determination!! Clearly the M.F. is not twice or three times the mass of the E.F.!!*

∴ M.F. = E.F.

= $C_{12}H_{36}O_4Si_5$

(c) STRUCTURAL FORMULA DETERMINATION:

* *This aspect of this question is asked very infrequently and has in this case many answers, one of which is indicated in the diagram below:*



TYPE EXAMPLE 2:

The mineral Azzurite is azure blue in colour and has a formula of $Cu_x(CO_3)_y(OH)_z$. When 2.0881g of finely crushed pure azurite is heated at 600 ^{0}C, 0.531g of carbon dioxide and 0.109g of water are produced; the black residue of copper (II) oxide weighs 1.444g.

(a) Use these data to calculate the EMPIRICAL FORMULA of azurite.

(b) Assuming azurite to be an ionic crystal, what species are in the crystal lattice? Show how these species are consistent with your formula.

* *T.E.E. 1998, Qu 5 Calculation.*

NB: $Cu_x(CO_3)_y(OH)_z$ could easily be re-represented as $C_yH_zO_pCu_x$ and in doing so becomes more recognisable as a standard empirical formula question.

SOLUTION

(a) EMPIRICAL FORMULA DETERMINATION:

$C_yH_zO_pCu_x$	+	O_2	→	CO_2	+	H_2O	+	CuO
2.0881g				0.531g		0.109g		1.444g

Step 1: Carbon Determination (Standard)

* CO_2
12.01
16.00 x 2
44.01 $gmol^{-1}$

$n(CO_2) = \frac{m}{M}$

$= \frac{0.531}{44.01}$

$\therefore n(CO_2) = 0.01207$ mol

$n(C) = n(CO_2)$

$\therefore n(C) = 0.01207$ mol

Step 2: Hydrogen Determination (Standard)

* H_2O
1.008 x 2
16.00
18.016 $gmol^{-1}$

$n(H_2O) = \frac{m}{M}$

$= \frac{0.109}{18.016}$

$\therefore n(H_2O) = 0.006050$ mol

$n(H) = 2 \times n(H_2O)$

$n(H) = 2 \times 0.006050$

$\therefore n(H) = 0.01210$mol

Step 3: Extra Element (non- standard)

* CuO
63.55
16.00
79.55 $gmol^{-1}$

$n(CuO) = \frac{m}{M}$

$= \frac{1.444}{79.55}$

$\therefore n(CuO) = 0.01815$ mol

$n(Cu) = n(CuO)$

$\therefore n(Cu) = 0.01815$ mol

Step 4: Mass Determinationof all Components (Standard)

$m(C) = n(C) \times M$

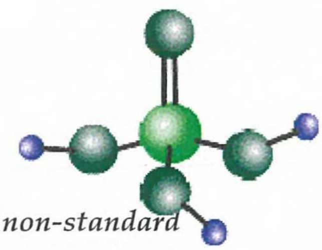
$= 0.01207 \times 12.01$

$\therefore m(C) = 0.1449g$

$m(H) = n(H) \times M$

$= 0.01210 \times 1.008$

$\therefore m(H) = 0.01219g$

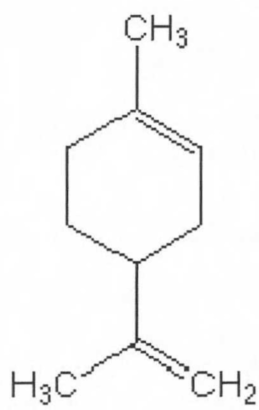


* *Determination of extra element is non-standard*

$m(Cu) = n(Cu) \times M$

$= 0.01815 \times 63.55$

$\therefore m(Cu) = 1.1534g$



Step 5: Determination of Oxygen (Standard)

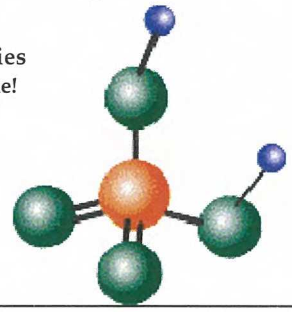
$m(O)$ = Total Mass of Compound Burnt - $m[C + H + {}^*Cu]$

$= 2.0881 - [0.1449 + 0.01219 + 1.1534]$

$= 2.0881 - [1.3105]$

$\therefore \underline{m(O) = 0.7776g}$

***Extra Element varies if indeed there is one!**



$n(O) = \frac{m}{M}$

$= \frac{0.7776}{16.00}$

$\therefore \underline{n(O) = 0.0486 \text{ mol}}$

Step 6: Mole Ratio (Standard)

	C	:	H	:	O	:	Cu * (Extra element varies!)
MOLE RATIO	0.01207	:	0.01210	:	0.0486	:	0.01815
**Division by smallest amount to simplify*	$\frac{0.01207}{0.01207}$	:	$\frac{0.01210}{0.01207}$	:	$\frac{0.0486}{0.01207}$	:	$\frac{0.01815}{0.01207}$
	1.00	:	1.00	:	4.02	:	1.50
**Multiplication by a factor to bring any number with a fraction to the nearest WHOLE NUMBER!*	(1.00	:	1.00	:	4.02	:	1.50 *) x 2
	2	**:**	**2**	**:**	**8**	**:**	**3**

$\therefore$ **Empirical Formula = $C_2H_2O_8Cu_3$**

The elements of the empirical formula could be re-arranged to form a compound of the general form : $\mathbf{Cu_x(CO_3)_y(OH)_z}$

$\therefore$ **Empirical Formula = $Cu_3(CO_3)_2(OH)_2$**

(b) Species present in azurite = Copper ions, Carbonate ions and Hydroxide ions.

VARYING APPROACHES TO DETERMINING EXTRA ELEMENTS

• I have seen questions where Nitrogen (N) is the extra element. The Nitrogen has been ***hydrogenated*** (had hydrogen added) which converts it to Ammonia (NH_3). The Ammonia is a ***basic*** gas which can then be ***titrated*** with a known hydrochloric ***acid*** solution. This allows the examiner to incorporate more than one type of calculation.

• I have likewise seen questions where Chlorine (Cl) is the extra element, which when ***hydrogenated,*** is converted to hydrogen chloride gas, that is in turn bubbled through water to make hydrochloric ***acid***. This acid can then be ***titrated*** with a ***base*** such as Sodium Hydroxide to determine the chlorine content, which is in a one to one ratio with the hydrogen content of the acid!

• ***Be careful*** in the second part of these questions where molecular formula is to be determined, that the **mass** of sample vaporized/analysed is the **same** as in part one of the question, where empirical formula is determined. This can be a trap!!